

Investigation and optimization of tin electrorefining in hydrochloric acid solutions

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Abstract High-tin containing soldering waste material could be recycled close to its origin on a flexible scale by electrolytic refining in pure hydrochloric acid–tin–chloride solutions. This method, offering potentially low costs, may become feasible by overcoming the difficulties of solution stability, electrolytic efficiency and deposit morphology. The tendency of the Sn(II) oxidation and precipitation can be overcome by properly controlling the concentration of the main components and the ratio of Sn(IV)/Sn(II) in the electrolyte solution. The virtual cathodic current efficiency can be increased above 90 % by assuring the dominance of Sn(II) species and optimising the composition of the electrolyte solution, the applied apparent current density and the parameters of the periodical current reversal. In the selected medium, the formation of chloro-complex ionic species may offer a beneficial level of natural inhibition. Organic additives exert no beneficial effect on any of the electrolysis characteristics. Applying a short cycle periodic current reversal technology is efficient in improving the morphology of the cathodic deposit. The loose structure of deposited metal requires special cell arrangement and care during operation. Electrolyte circulation does not affect current efficiency significantly. It should be applied in practice for the control of composition. The attainable purity is close to 99.99 %, which greatly surpasses the technical standards.

Keywords Soldering scrap · Electrorefining · HCl solution · Precipitation · Polarization curves · Current efficiency · Cathode morphology · High purity

1 Introduction

During the operation of the lead-free tin soldering bath, the copper concentration is steadily increasing. Beside dross formation, this is the main cause for the high amounts of soldering scrap. This material may also contain significant amounts of iron, silver, bismuth and antimony. Electrolytic refining—although less commonly applied for tin—can achieve efficient purification in one step. Impurities of characteristically higher electrode potential (Cu, Ag, Au, Bi, Sb, As,) practically do not dissolve from the anode, but they build a fine slime at the surface, in the elemental or oxide form [1]. Due to the uneven dissolution, the anode slime contains significant amounts of tin powder. This can be considered as a by-product, suitable for silver extraction. Lead and tin have similar standard potentials, therefore lead could dissolve from the anode and deposit to a significant degree at the cathode. However, modern soldering scrap is generally lead-free, and the lead concentration in the solution is marginally low. Metals of more negative electrode potentials (Zn, Fe, etc.) can dissolve but they will not deposit at the cathode, unless their concentration increases beyond a certain limit dependent on the actual concentration of tin at the cathode surface.

Acid electrolyte solutions are favourable for tin electrorefining because of the predominantly divalent form of dissolved tin. However, a large amount of anode slime is generated with high tin content and it is almost impossible—even with the application of organic additives—to obtain a dense cathodic deposits [2]. The relatively scarce

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industrial applications are based on the application of sulphuric acid in a multi-component bath, containing approximately 30 g dm^{-3} tin as SnSO_4 , cresylic-phenylic sulphonic acid ($40\text{--}100 \text{ g dm}^{-3}$) and free sulphuric acid ($40\text{--}80 \text{ g dm}^{-3}$) with $1\text{--}2 \text{ g dm}^{-3}$ naphthol, or gelatine also added [3]. The acid assures hydrolytic stability, improves conductivity and reduces the solubility of lead. Cresylic-phenylic sulphonic acid is extremely expensive, but it is necessary to improve solution stability through more soluble compounds of Sn(IV), whereas naphthol or gelatine promote finer structures of the cathodic deposit. Simple sulphuric acid- SnSO_4 electrolyte solutions have also been tested, however they allow inferior stability and cathode quality, only slightly improved by applying the PCR technology [4].

The application of pure HCl-SnCl_2 solutions is definitely preferred if tin of high purity is the aim. Any chlorine entrapped in the cathode is removed by the final melting step to obtain a compact product. Addition of organic agents to the electrolyte solution may be omitted, as Sn(II) forms very stable chloro-complex ions, which may result in a favourable natural inhibition, controlling the fast electric charge transfer step and thus helping to avoid the growth of extremely rough crystals [5]. The solubility of tin in chloride media is very high [6] and productivity is greatly increased by the applicability of higher current densities. Conductivity of the solution and the growth rate of the crystals are high, therefore electricity cost is next to negligible. Nevertheless, the cathodic deposit is rough and dendritic, requiring special provisions for avoiding short cuts. The current efficiency is reduced by the aggressive effect of Sn(IV) and possible hydrogen evolution. All these aspects require experimental investigations and optimization of the electrolysis parameters. However, the basic problem to overcome before any electrolysis can be started is solution instability.

The standard potentials ($\text{Sn}^{4+}/\text{Sn}^{2+} = 0.154 \text{ V}$ and $\text{Sn}^{2+}/\text{Sn} = -0.136 \text{ V}$) suggest that Sn^{2+} can be stabilized in aqueous solutions. However, the formation of chloro-complex ions may modify the distribution of tin between the two possible oxidation states. The computer program ROCC developed at our department was used in modeling the conditions mathematically. The algorithm of the simulation [7] is based on the electrode potentials of the aquo-ions and the stability constants of the chloro-complex species [8] included in the program's data base. The distribution of tin among the various species in contact with metallic tin or air in solutions of varied chloride ion concentrations is shown by the plots in Fig. 1, representing our results of the mathematical simulation. The Sn(II) solution has a good stability in contact with metallic tin over the entire Cl^- ion concentration range, but it may be easily

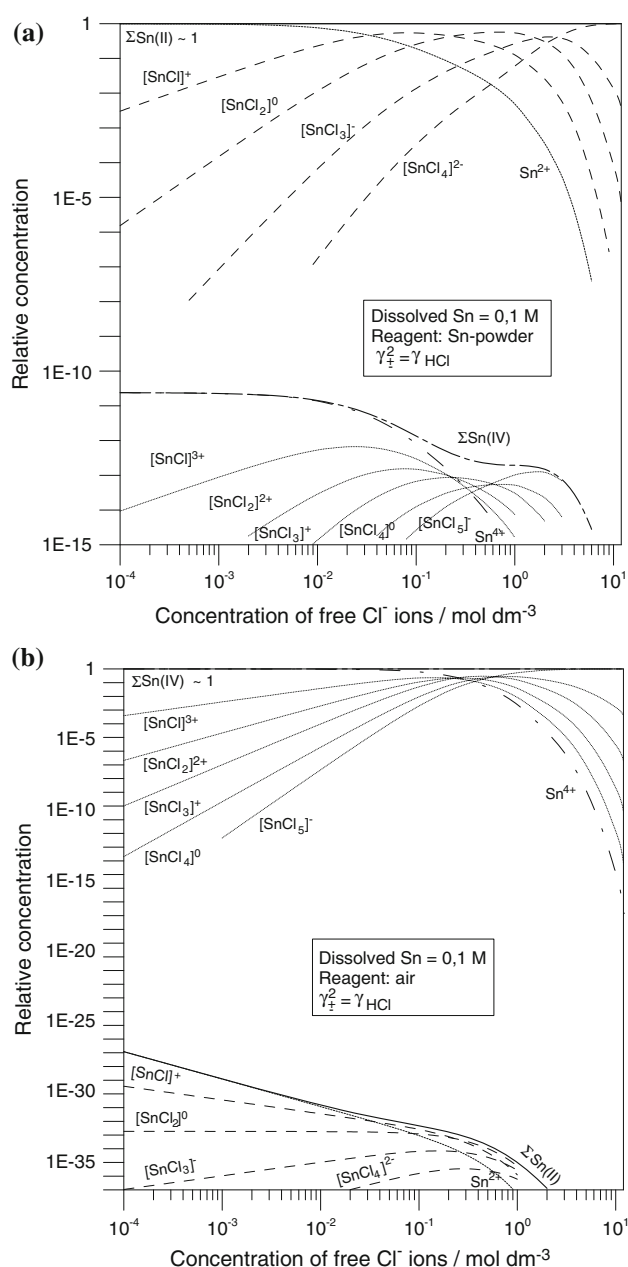
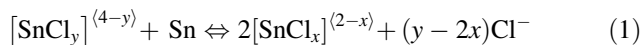


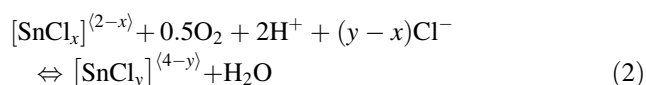
Fig. 1 Equilibrium distribution of Sn among different species dissolved in HCl solutions in contact with **a** tin metal, or **b** air

oxidized if the redox potential is determined by oxygen in air.

The reaction



ensures the stability of the Sn(II) form in regions of the solution in contact with metallic tin. This also implies some re-dissolution of the metal deposited at the cathode, thus it can reduce the current efficiency too. On the other hand, some Sn(IV) ions can be formed locally by the oxidizing effect of air or the anode:



Stability of the various species in the tin-chloride-HCl solution at any possible redox conditions can be outlined by potential— pCl^- plots. For constructing such a diagram, shown in Fig. 2, we have determined the equilibrium potentials as functions of the chloride ion activity, assuming unit activities of the chloro-complex tin species and applying the standard electrode potentials (vs. SHE) of the aquo-ions and the complex stability constants [8].

The possible rate of Sn(II) oxidation in stationary solutions may be of practical interest for the process. We have applied a method using the corresponding changes in the light absorption spectra—obtained with a Shimadzu UV1601 spectrophotometer—of the Sn(IV) species. A differential method using phenyl fluoron indicator [9] proved to be suitable for a qualitative indication. For quantitative analysis, however, we used the direct iodometric analysis of Sn(II) concentration. The total tin concentration was determined by the same method after a complete precipitation and re-dissolution of tin under nitrogen atmosphere in boiling 6 M HCl assisted with platinum catalyst. The corresponding photometric and iodometric results in Fig. 3a, b show the continuous but relatively slow generation of Sn(IV) in contact with air. If the open solution is kept in contact also with metallic tin, the Sn(IV) concentration is relatively stable, but the total

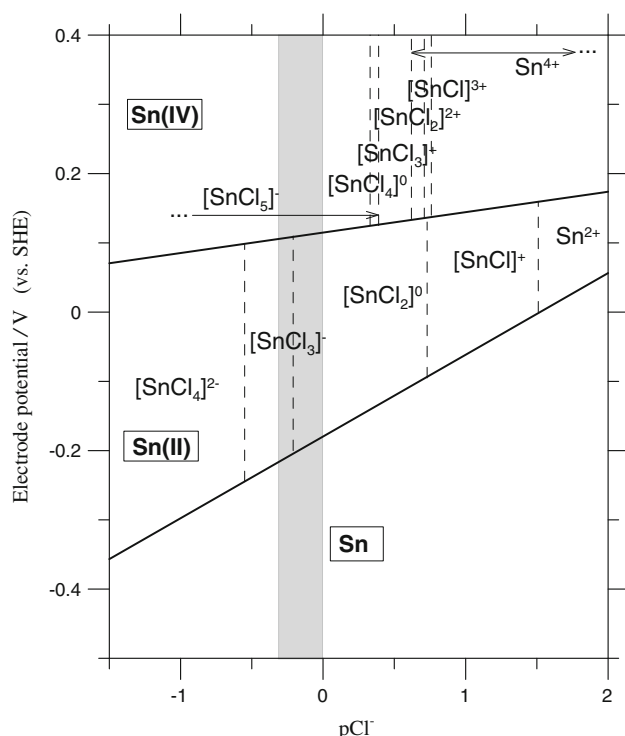


Fig. 2 Predominance of species in the Sn-H₂O-Cl system

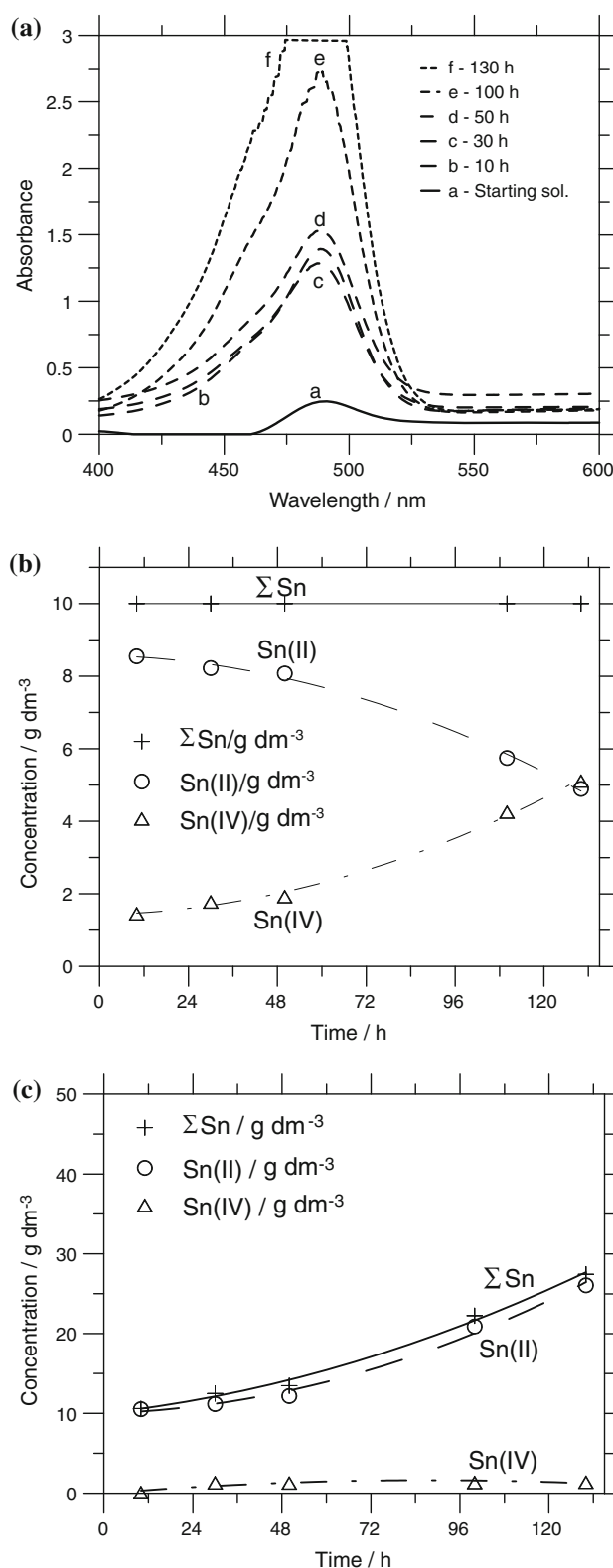


Fig. 3 Changes in the concentrations of Sn species in the 1 M HCl-tin-chloride solutions during long time standing **a, b** in contact with air, **c** in contact with air and metallic tin

Sn concentration increases by the combined effect of reactions (1) and (2), as represented by Fig. 3c. Although the oxidation by air is relatively slow, it may cause eventually instability of the solution, especially when the tin concentration becomes high. At lower Cl^- and appreciable OH^- ion concentrations, tetravalent tin may form stable hydroxide or oxide compounds, resulting in white–yellow stannic acid type ($\text{SnO}_2 \cdot n\text{H}_2\text{O}$)-precipitations [9]. In the 1–2 M HCl concentration range, $\text{Sn}(\text{OH})_4$ is not formed but SnO_2 may arise if the electrode potential is higher than ~ 0.15 V (vs. SHE) [10]. Therefore, the area of the anode and the surface of the solution may be affected by the formation of hydrated stannic oxide precipitation. We have examined the precipitated particles by X-ray diffraction. The obtained diffraction pattern (Fig. 4) demonstrated the presence of $\text{Sn}_6\text{O}_4(\text{OH})_4$ and SnCl_2 . Preferring the lowest possible HCl concentration for application, 1 M HCl solutions have been in the focus of further attention. Therefore, the electrolytic refining of tin in HCl solutions requires counteracting the tendency of $\text{Sn}(\text{II})$ oxidation and the control of Sn concentration at the same time.

2 Experimental procedure

The current obtained at the tin cathode or anode during the initial stages of the electrolysis was studied by the potentiodynamic technique. The main characteristics of electrodeposition were examined as functions of the solution and current parameters in long-term electrorefining runs in laboratory cells. The electrolyte solutions were generally prepared by using boiling 6 M HCl to dissolve the required amounts of tin powder to produce 150 cm^3 batches with 5,

10, 20, 30 and 50 g dm^{-3} Sn concentration. The reactor flask was equipped with a reflux condenser. Dissolution was enhanced by a platinum mesh also added to the flask. The different final HCl concentrations were set by dilution with the proper amounts of 6 M HCl and distilled water. The resulting concentration ratio of $\text{Sn}(\text{IV})/\text{Sn}(\text{II})$ was found usually ~ 0.05 in the prepared fresh electrolyte solution.

2.1 Potentiodynamic experiments

The anodic dissolution of the metal and the cathodic reduction of the ions were studied in a setup designed to approximate the conditions in practical electrorefining. Beside the saturated calomel electrode (SCE) reference, the counter electrode was a Pt spiral and a small tin plate with 1- cm^2 prepared surface was used as the working electrode. The apparent current density refers to the geometric surface area of the fresh electrode. Agitation of the solution was possible by a 2.5-cm magnetic stirrer bar at the bottom of the 100- cm^3 thermostated triple-neck cell of the usual layout. During cathodic polarization, the actual surface of the electrode increased due to coarse deposition, just as in the case of the actual electrolysis. The voltage between the working and the reference electrode was controlled by an Electroflex EF 435C potentiostat. The generated current was recorded by the attached computer using EF 2105 AD/DA converter interface. The measurements started from zero current equilibrium potential. The measured data were registered after 5-s setting time at every potential step.

2.2 Electrorefining experiments

The anodes were cast from the scrap tin obtained from JABIL-Hungary Electronics Co. The starting cathode was prepared by forming—by pre-electrolysis—a thin compact tin layer on a masked copper plate and polished to approximately the same surface quality before every run. The other parts of the plate around the 9- cm^2 square open surface area (Fig. 5a) were covered with a lacquer layer and a polyethylene foil. The experimental cell—made from a suitably thick polycarbonate plate—is schematically shown in Fig. 5b. An inserted fine filter mesh separated the anodic and cathodic compartments, helping to avoid the contact between the roughly growing deposit and the slimy anode surface. The long dendritic outgrowths were periodically pressed back by a gentle touch of a Teflon spatula. Two regulated DC (direct current) current supplies—connected in opposite directions—were used for the experiments with PCR current. They were periodically switched over by a computer controlled switching device developed in our laboratory. The most usually applied PCR settings were 4 s forward and 0.2 s reverse periods of the same

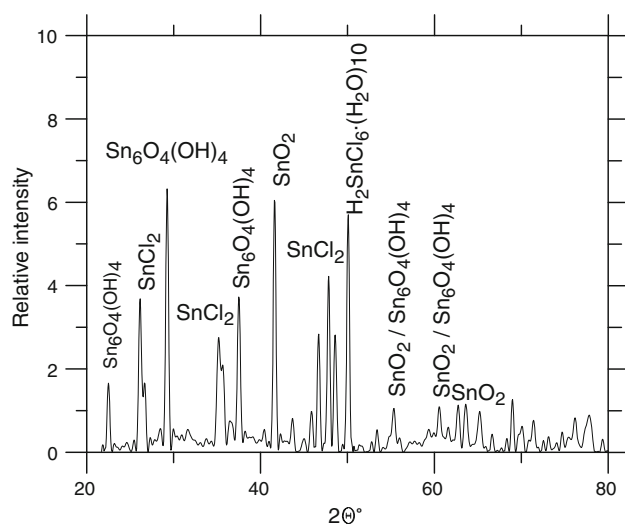


Fig. 4 The X-ray diffraction analysis of the precipitation formed by keeping the tin-chloride–1 M HCl solution in contact with air and tin metal for a prolonged time

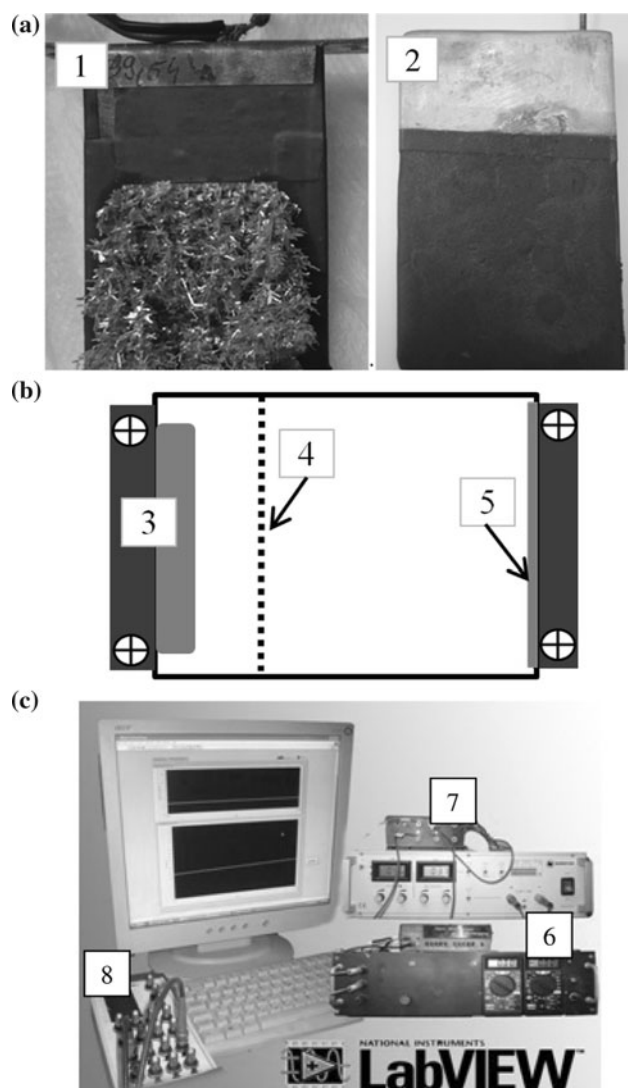


Fig. 5 The electrolysis equipment, **a** electrodes, **b** cell and **c** current control and data acquisition (1 cathode plate, 2, 3 anode, 4 mesh separation, 5 cathodic deposit, 6 current supplies, 7 PCR switching unit, 8 converter interface)

absolute current. Voltage and current data were recorded by a computer equipped with a National Instruments NI-USB 6212 AD/DA interface and the NI Labview 8.5 software for data acquisition and processing (Fig. 5c). In order to assess the efficiency of the cathodic process, the deposit was regularly removed during the electrolysis and measured after washing and drying.

3 Experimental results and discussion

3.1 Potentiodynamic experiments

The anodic and cathodic polarization curves in Fig. 6a, b show that the electrode processes allow relatively high

currents even in stationary solutions of relatively low tin concentration. There is some passivation observed at ~ 1 V above the equilibrium potential. It does not interfere with the possible range of operation and is moved even further away by increasing stirring intensities beyond 200 revolutions per minute (r.p.m.). The initial peak of the cathodic polarization curves is clearly visible in the stationary or the mildly stirred solutions. The tin plate immersed in the solution is attacked by Sn(IV). Before the start of the cathodic reduction, the local concentration of Sn(II) is increased through the spontaneous dissolution

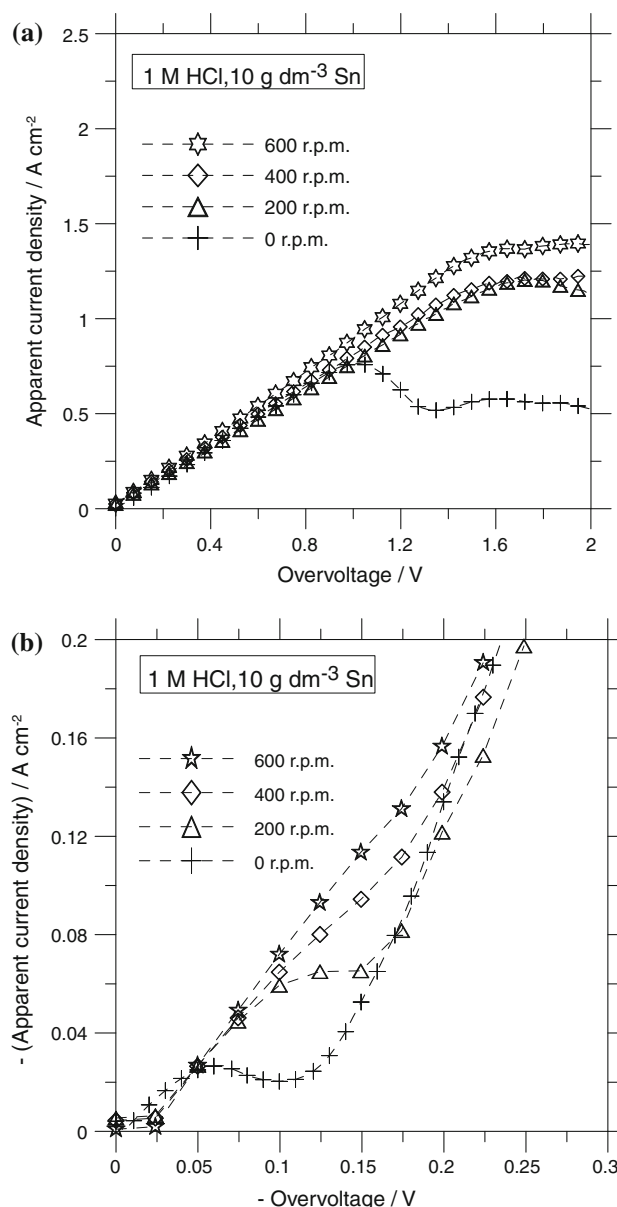


Fig. 6 Anodic (**a**) and cathodic (**b**) polarization curves at different rates of stirring

reaction of Eq. (1). Therefore, the initial section of the polarization curve corresponds to a locally higher tin concentration. Agitation—started before increasing the cathodic potential—disperses the dissolved tin ions, therefore the initial effect is relatively lower, but the effect lasts longer. Later sections of the polarization curves (from about $1,000 \text{ A m}^{-2}$) are only slightly different at increasing stirring rates. These results suggest that the planned electrorefining process can be implemented in quasi-stationary solutions, agitated only by the forced circulation required for the stabilization of solution parameters.

Cathodic polarization curves obtained at varied tin or HCl concentrations are shown in Fig. 7. In stationary solutions, the initial peak of the cathodic current is clearly seen at low total tin concentrations (Fig. 7a). At higher total tin concentrations, the effect of the preliminary local concentration rise is relatively lower, but due to the also higher Sn(IV) concentration, this may last longer. At $\sim 1,000 \text{ A m}^{-2}$ apparent current densities, all the curves in the $10\text{--}50 \text{ g dm}^{-3}$ Sn concentration range are in a $\sim 40 \text{ mV}$ wide overpotential range. Lower tin concentrations may cause higher risk of H^+ ion reduction, higher tin concentrations may imply higher risk of precipitation formation. In view of a fast rate of metal deposition, low hydrogen evolution and solution stability, 10 g dm^{-3} tin concentration may be a practical setting. The current attributed to the deposition of hydrogen at the original surface of the tin working electrode is shown in Fig. 7b. It was found negligible at all the examined cathodic potentials below 2 mol dm^{-3} HCl concentrations. In solutions containing also tin (Fig. 7c), the steep and steady rise of the apparent current density associated with the reduction of Sn(II) is enhanced by the deposition of tin in a rough dendritic form, increasing the effective cathode surface. At higher cathodic overpotentials, when the cathode surface has become rougher, the actual current densities are lower than the apparent values obtained from the original (geometric) surface. The 0.5 M HCl concentration causes instability, rendering part of the content inactive, therefore the corresponding curve is lower than the rest of the quite uniform curves at higher HCl concentrations. In the 1 M HCl solution, the obtained currents are significantly higher than those at corresponding overpotentials in the 0.5 M HCl solution. As hydrogen evolution could not be observed, this is caused by the increased activity of dissolved tin. On the other hand, hydrogen evolution could be observed at even higher acid levels. As the deposited tin increased the effective cathode surface, hydrogen evolution could start earlier than suggested by Fig. 7b. With respect to the activity of dissolved tin and the cathodic evolution of hydrogen, 1 M HCl can be considered as a good choice for the refining process.

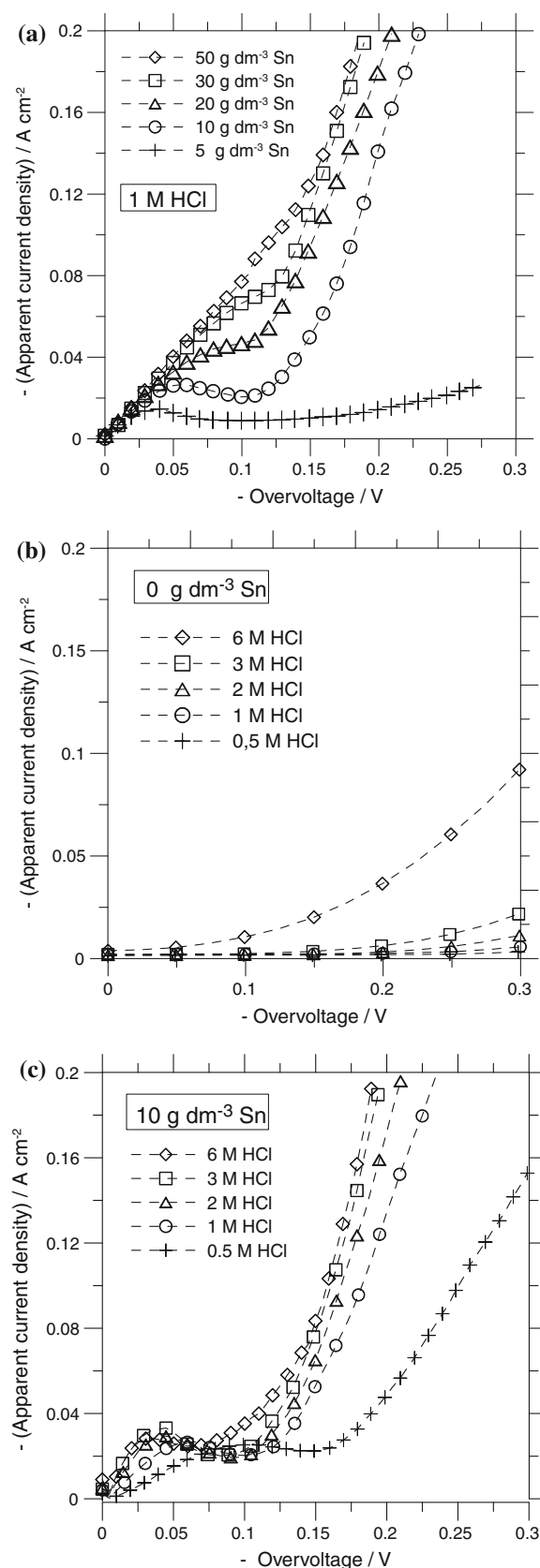


Fig. 7 Cathodic polarization curves obtained with stationary electrolyte solutions containing different concentrations of Sn and HCl

Fig. 8 The observed current efficiency as a function of **a** the cathodic current density (1 M HCl, 10 g dm⁻³ Sn) **b** the tin concentration (1 M HCl, $I_+ = I_- = 1,000$ A m⁻²) and **c** the hydrochloric acid concentration (10 g dm⁻³ Sn, $I_+ = I_- = 1,000$ A m⁻²)

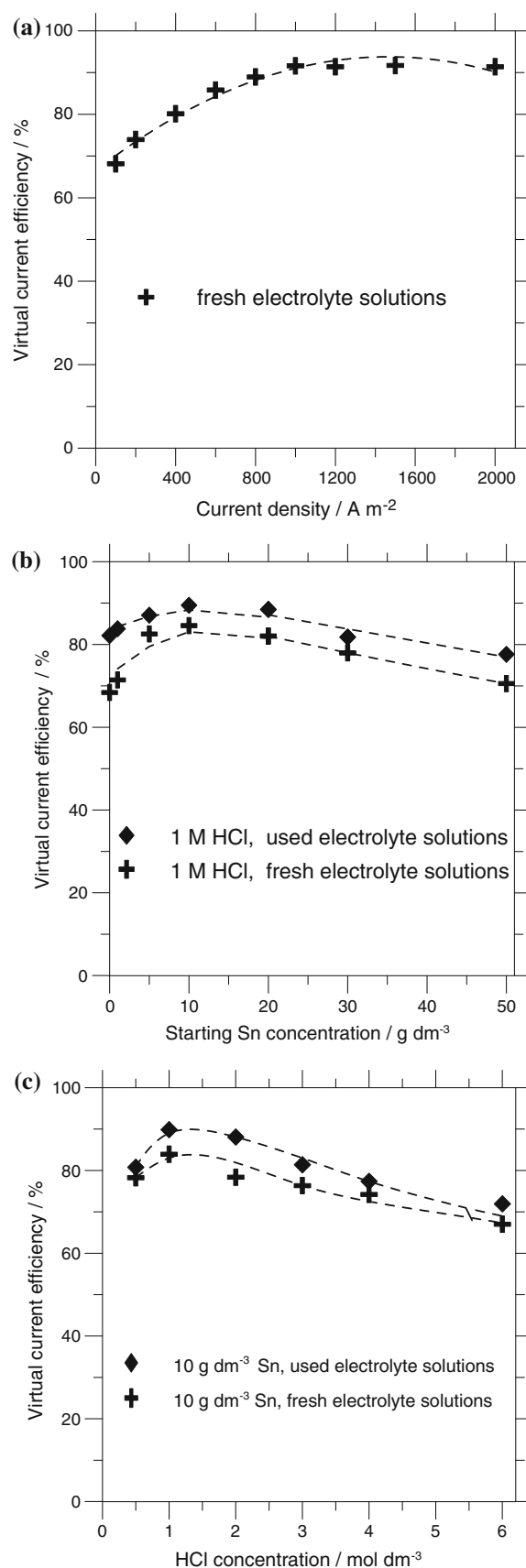
3.2 Electrefining experiments

The current efficiency may be significantly reduced by the corrosive effect of the Sn(IV) ions, expressed in Eq. (1). It may be also reduced by the simultaneous reduction of hydrogen ions at higher than optimum current densities. This is reflected in the gross current efficiency, expressing the utilisation of the total electric charge

$$H_{\text{gross}} = \frac{\frac{zF}{A_{\text{Sn}}} \Delta m_{\text{Sn}}}{\int_{t_s}^{t_e} \left(\frac{t_+}{t_+ + t_-} I_+ + \frac{t_-}{t_+ + t_-} I_- \right) dt}, \quad (3)$$

where Δm_{Sn} is the mass increment of the cathode in the $(t_e - t_s)$ interval, I_+ and I_- are the absolute forward and reverse currents in the t_+ and t_- corresponding periods, F is the Faraday constant z is the valence of the electroactive ions and A_{Sn} is the atomic mass. A virtual value of the determined current efficiency was expressed assuming the deposition of the—generally predominant—Sn(II) species. Thus with the applied PCR settings of $t_+/t_- = 20$ and $I_+ = I_-$ the maximum gross current efficiency can be 90.5 % if only Sn(II) species are reduced at the cathode. Figure 8a shows that increasing the apparent current density until $\sim 1,000$ A m⁻² significantly increases the virtual gross current efficiency. Beyond this value hydrogen evolution hinders the further increase of the virtual current efficiency. Therefore, this is preferred as a practical setting.

The effects of the tin and hydrochloric acid concentrations have also been explored by the long-term experiments. The results in Fig. 8b demonstrate that the optimum tin concentration can be 10 g dm⁻³. This result confirms the findings of the potentiodynamic experiments. When the solution did not contain tin initially, the virtual current efficiency was below 70 %, mostly due to the intensive hydrogen evolution. However, the instant cathodic deposition of the anodically dissolved tin was possible. On the other hand, increasing the tin concentration beyond 20 g dm⁻³, the corrosive effect of the increased amount of Sn(IV) may have reduced the current efficiency causing more re-dissolution of the deposit by Eq. (1). In case of the hydrochloric acid concentration, the 1–2 M HCl seems to be the optimum. It corresponds fairly well to the conclusions drawn from the results of the potentiodynamic experiments. Under 1 M HCl concentration, the tin solutions can easily lose their stability. Higher HCl concentrations than 2 M result in decreasing current efficiencies because the higher concentration of H⁺ ions enhances H₂ evolution and the solubility of the corrosive Sn(IV)



increases through the stabilization of chloro-complex species (Fig. 1). In comparison of the two consecutive runs, fresh solutions proved slightly less efficient, because the inadvertent Sn(IV) concentration is higher directly after dissolution.

The effect of the cycle time ratios applied for the PCR and intermittent (periodically stopped) current were also investigated. Figure 9a, b shows that increasing cycle time ratios (t_+/t_-) result in the expected higher current efficiencies. With relatively longer forward current periods, the forced or spontaneous re-dissolution of the cathodic deposit during the reversed cycles is depressed. Application of the DC current on a long run, however, may result in further difficulties caused by the rough crystal structure.

In simple electrolyte solutions, applying stronger circulations improve performance through enhanced mass transport. However, as shown by the results in Fig. 9c, this is virtually ineffective in this case. Stronger circulation increases the rate of reaction (1), therefore the current efficiency is slightly reduced by intensified re-dissolution, especially in the fresh solutions, where the Sn(IV) concentration can be higher. The only benefit of the stronger forced circulation may be the limiting of the outgrowing Sn

crystals. The influence of temperature is shown in Fig. 9d. As a result of contrary effects of lower polarization and higher rate of re-dissolution, the current efficiency is little affected by varying the solution temperature around 25 °C.

The effect of adjusting the PCR/intermittent current time parameters on the refinement of the crystal structure was also examined. Lower cycle time ratios (t_+/t_-) proved slightly more efficient in improving the morphology of the generally rough electrocrystallization, as shown by the structural photographs of Fig. 10a taken after the initial 15 min of electrolysis. Figure 10b shows the deposit obtained in 2 h continuous electrolysis. Strong re-dissolution—corresponding to low current efficiency—can be observed at the center of the cathode at a low cycle time ratio (t_+/t_-) of the PCR or intermittent current, although the structure is more refined. However applying higher t_+/t_- cycle time ratios than 20 does not increase current efficiency, but causes more irregular crystal formation. Probably, the higher effective anode potentials—generating more Sn(IV) species—and the rougher cathodic deposit structures—promoting re-dissolution—prevent the current efficiency from further increasing. It may indicate the significance of the anodic reaction as a possible source of

Fig. 9 The effect of the cycle time ratio of **a** the periodically reversed or **b** intermittent current and **c** the circulation velocity and **d** temperature on the virtual current efficiency (apparent current density $1,000 \text{ A m}^{-2}$, 10 g dm^{-3} Sn, 1 M HCl , 2 h electrolysis time)

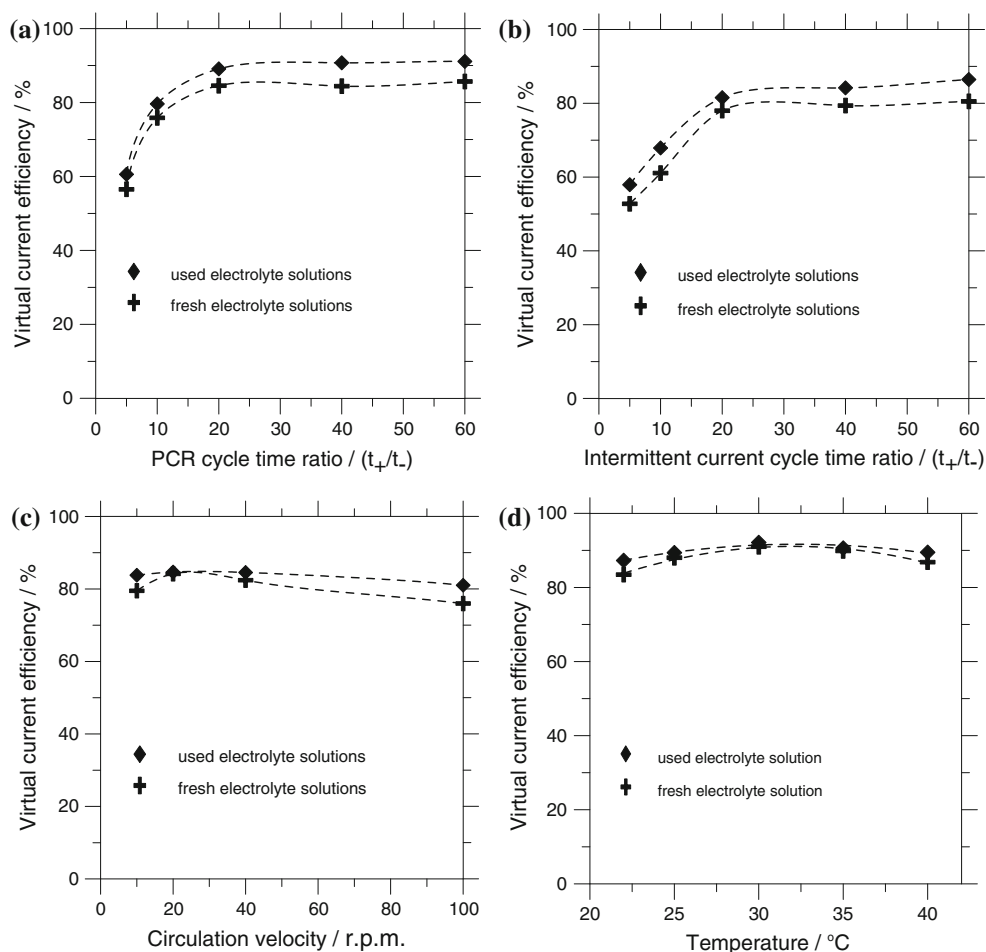
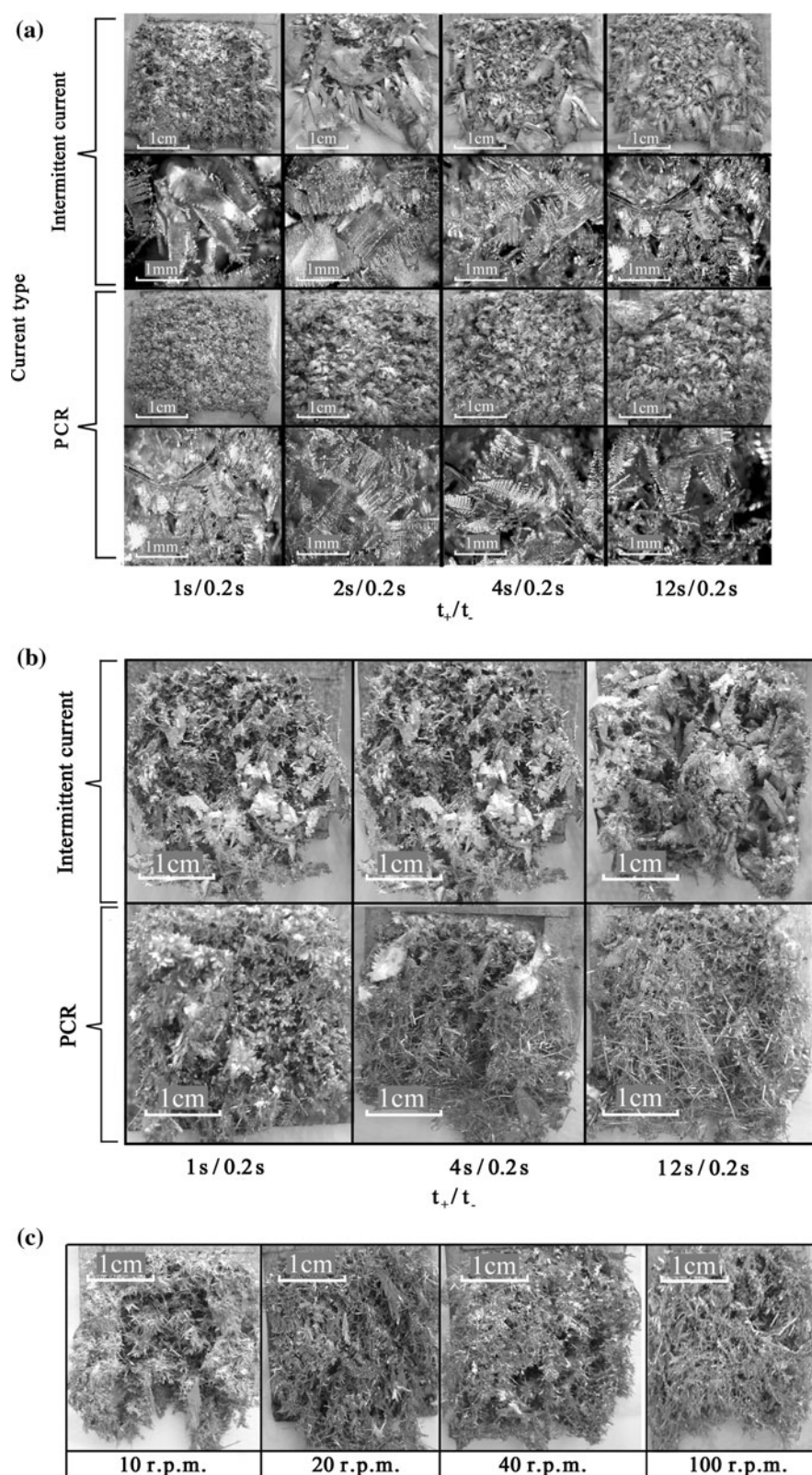


Fig. 10 The characteristic structures of cathodic deposits obtained with $1,000 \text{ A m}^{-2}$ apparent current density and **a** different PCR and intermittent current times (electrolysis time 15 min), **b** different PCR and intermittent current cycle time ratios $t_+/t_- = 5-20-60$ (electrolysis time 2 h) and **c** agitation with 10, 20, 40, 100 r.p.m. magnetic stirring (PCR cycle time ratio $t_+/t_- = 4 \text{ s}/0.2 \text{ s}$, electrolysis time 2 h)



Sn(IV) species. At lower cycle time ratios than 20, the cathodic deposit does not get finer, but significantly more deposited tin is re-dissolved. Therefore, the cycle time ratio

of ~ 20 may be considered as optimum when the intensities of the forward and reverse currents are identical. When the current is only interrupted periodically, the effects are

similar to those obtained with PCR applying the same current density in the reverse direction, but the average current efficiency was found lower. Increasing the rate of stirring had no beneficial effect on the obtained structure (Fig. 10c).

The effect of 0.267 g dm^{-3} gelatine addition to the freshly prepared electrolyte solutions was tested with the 1 M HCl , $10 \text{ g dm}^{-3} \text{ Sn}$ freshly prepared solutions applying $1,000 \text{ A m}^{-2}$ apparent current densities and PCR. As a result of gelatine addition, the virtual cathodic current efficiency was reduced by $\sim 3 \%$. This can be attributed to the polarizing effect of the organic inhibitor, resulting in the generation of more Sn(IV) at the anode. This finding is confirmed by the measured increase of the total tin concentration to 11 g dm^{-3} without and to 12 g dm^{-3} with gelatine addition from the starting value of 10 g dm^{-3} in the 2 h electrolysis, while the HCl concentration remained unchanged. Iodometric analysis proved, that the increment is in the form of Sn(II) , therefore the generated Sn(IV) could be continually consumed in contact with metallic tin by reaction (1). The addition of gelatine—as an inhibitor—has slightly unfavourable effects both on the current efficiency and the stability of the tin concentration. We have also tested the application of argon atmosphere in a specially devised closed electrolysis cell. The results were only slightly better. This corresponds to the slow oxidation rate (Fig. 3) of dissolved Sn(II) in contact with air. During electrolysis, the majority of the harmful Sn(IV) species may be generated at the anode and not at the open surface of the electrolyte solution.

In further examining the effect of gelatine addition, the anodic and cathodic overpotentials were measured against calomel reference electrodes equipped with Luggin-capillaries. Figure 11 shows that polarization is slightly decreasing with electrolysis time and increased by the incorporation of gelatine in the electrode surfaces. The effect of the colloid additive is clearly reflected in the observed overpotentials and the current efficiency was slightly deteriorated. However, the expected beneficial effect of gelatine on the morphology of the cathodic deposit was not observed. As Fig. 5a has shown, the anodic reaction is undisturbed in the range of the actual overpotentials. Also, the acid concentration was found approximately stable, thus hydrogen evolution may be less significant in determining the cathodic current efficiency. It confirms the importance of curbing the generation of Sn(IV) species during the operation.

The obtained crystal structures can be arranged according to the relative current density, expressed as the ratio of the current density (J) to the limiting current or to the tin concentration (c_{Sn}) and the applied level of inhibitor addition in a system suggested by Winnand [11]. As Fig. 12 shows, tin typically crystallizes with the unfavourable field-oriented isolated (FI) structure with dendritic crystals in the

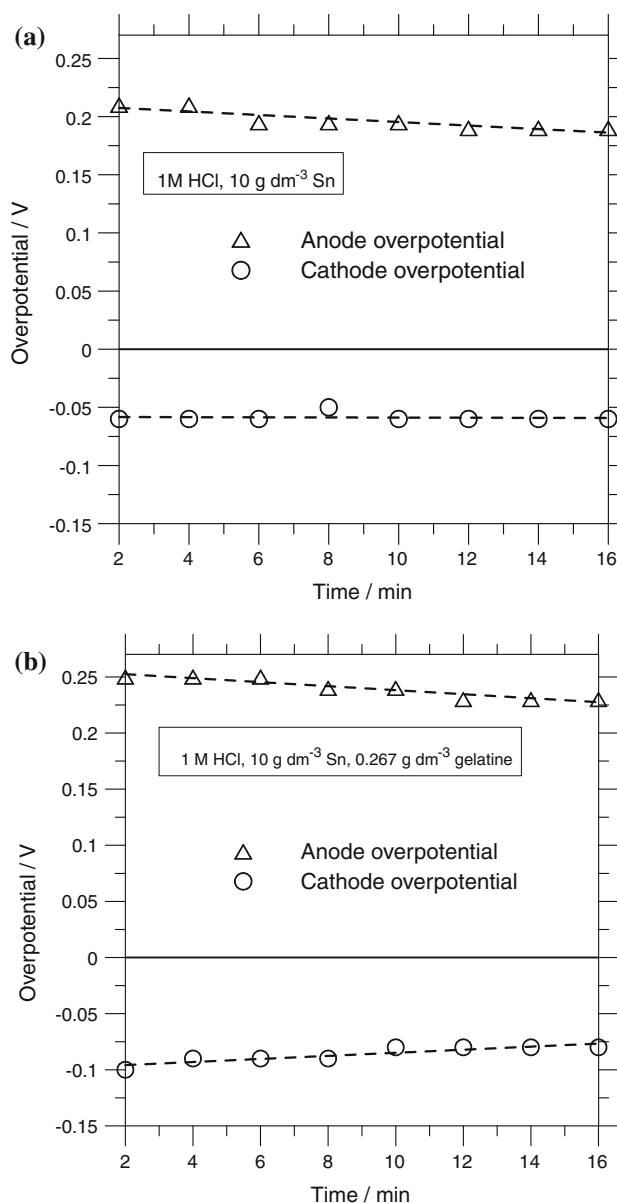


Fig. 11 The overpotentials of the electrodes in 1 M HCl electrolyte solutions **a** $10 \text{ g dm}^{-3} \text{ Sn}$, **b** $10 \text{ g dm}^{-3} \text{ Sn} + 0.267 \text{ g dm}^{-3} \text{ gelatine}$ ($1,000 \text{ A m}^{-2}$)

whole-examined range of current density to tin concentration even with the addition of a significant amount [1, 3] of gelatine. Neither increased starting Sn -concentrations nor gelatine additions could result in a different crystal structure. Therefore, the filter mesh separation between the anode and the cathode compartments and occasional mechanical compacting of the cathode deposit may be useful in practical application. The dendritic electrocrystallization is linked to loose adherence of the deposit, which makes its easily removable from the cathode plate.

The main impurity, copper is almost completely retained in the anode slime. The rest of the impurities are also

Fig. 12 Typical morphologies of the cathodic deposit in pure and gelatine-containing electrolyte solutions in function of the relative current density (ratio of the current density to the tin concentration) and the applied inhibition (PCR, $I_+ = I_-$, 4 s/0.2 s, 1 M HCl, 15-min electrolysis time)

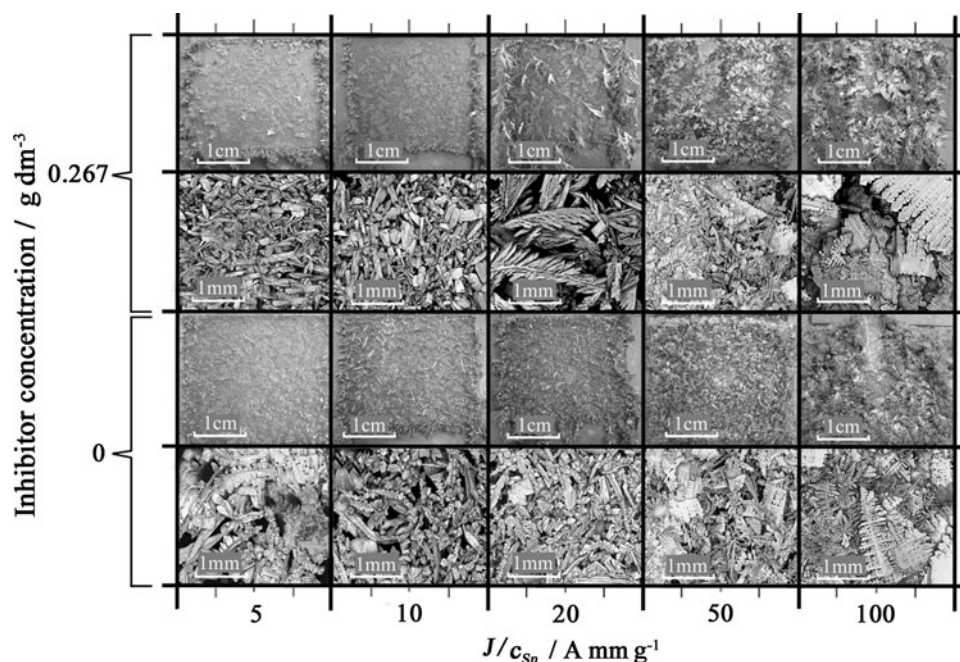


Table 1 Analysis of the impure anode and the purified cathode deposit

	Concentration (%)							
	Ag	Al	As	Bi	Cu	Fe	Pb	Sb
Anode	0.0805	2.1442	0.0030	0.0414	1.9605	0.0050	0.0187	0.0367
Cathode-4 h	0.0019	–	0.0002	0.0008	0.0249	0.0004	0.0010	0.0005
Cathode-8 h	0.0004	–	0.0001	0.0004	0.0063	0.0004	–	0.0003

separated. The efficiency of purification can be assessed by comparing the compositions of the anode made of the raw material and the produced deposit at the cathode. Table 1 shows the impurity concentrations in the cathode deposits corresponding to the process characterized by Fig. 8a. The most important impurities in the tin soldering scrap are efficiently removed by the optimized electrorefining procedure.

4 Conclusions

Recovery of the valuable tin content and the elimination of the usual copper impurity from the lead-free soldering scrap can be achieved by electrorefining. With the purpose of providing the basis for a cost efficient novel technology applying pure HCl solutions, the known difficulties caused by uncertain stability, low current efficiency and rough morphology of the cathodic product have been investigated. The results could be used for devising the process under practically optimized conditions. Stability of the tin chloride–HCl solution can be assured by controlling the

concentration of Sn(IV) and the total tin content. Potentiodynamic experiments have shown that 1 M HCl and 10 g dm^{-3} Sn stationary electrolyte solutions can be applied to advantage. High virtual current efficiencies could be reached with apparent current densities of approximately $1,000 \text{ A m}^{-2}$, applying the PCR technology with 20:1 cycle time ratio and equal intensities of forward to reverse currents. Experiments have proved that forced circulation or organic additives may not improve the main characteristics. The morphology of the cathodic deposit consists of typically field oriented isolated dendrites and it cannot be much improved. However, the purified product is easily removed and melted submerged in a liquid tin bath. All the important impurities are separated either by the selective anodic dissolution or the preferential cathodic deposition. The favorable performance of the HCl-based electrolyte solution has proved the expected beneficial effects of complex formation, high solubility and suitable electrode processes. The possible low costs of operation and high value of the purified tin produced may justify considerations of industrial implementation. The method allows flexibility also in terms of production scale.

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